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Water leaching of cesium from selected cesium mineral analogues

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Abstract

Recently, a new mica phase Cs-tetra-ferri-annite has been synthesized and studied. This phase has been investigated because its high structural stability and assumed associated low leachability for Cs suggest that it may be a suitable waste form for immobilization of Cs. Further, synthesis, under hydrothermal conditions, is possible under conditions typical of an industrial-scale immobilization plant. Consequently, cesium-tetra-ferri-annite can be considered as a waste form for the fixation of Cs from solid radioactive waste. In this study, Cs immobilization in Cs-tetra-ferri-annite and $CsAlSiO_4$, as well as sorption onto montmorillonite and zeolite 13X, have been studied. Experiments were carried out to determine the influence of pH, temperature, time and leaching technique on the extent of release of Cs from these solids. These leaching studies have confirmed the limited leachability of Cs-tetra-ferri-annite, which was found to be more stable than $CsAlSiO_4$ by a factor of 3.7 at ambient temperature and near-neutral pH. These waste forms have also been found to be more effective in retaining Cs than Cs-montmorillonite and Cs-zeolite 13X. The relative release of Cs from all of the studied phases exhibits a similar trend with pH, temperature, time and techniques of leaching used in this study. For these phases, the leachability of Cs increases with acidity (pH 3) or alkalinity (pH 11) of the leachates as well as with increasing temperature and time of leaching. For $CsAlSiO_4$, the Cs-leachability was most strongly affected by increasing temperature. Cesium releases from this phase increased by a factor of about 6 when the temperature was raised from 20 to 100 °C. This increase with temperature was 3–6 times higher than that measured for the other phases. Under the present leaching conditions, Cs is released more than the matrix elements. Elements present in tetrahedral positions of $CsAlSiO_4$, Cs-montmorillonite and Cs-zeolite 13X leach much easier than elements in octahedral positions.
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1. Introduction

The disposal of radioactive Cs waste is an important issue, because Cs may be released from nuclear power plants and/or temporary radwaste deposits as in Chernobyl (Zachara et al., 2002) and/or in Hanford-like events (e.g. Zachara et al., 2002; Flury

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et al., 2004; Liu et al., 2004). Only very few inorganic structures are capable of strongly fixing this low-charge, large cation with an ionic radius close to 0.18 nm. As a consequence, water easily leaches out Cs from most known Cs-containing materials. Subsequently, Cs is easily transported through contact with water, adsorbed on soils and transferred to the biosphere (Gutierrez and Fuentes, 1996; Hsu and Chang, 1994; Dumat et al., 2000). Cesium in nuclear power plants is primarily contained in the nuclear fuel. During fuel re-processing Cs is present in the liquid HLW and this waste can be incorporated into glass or other high level waste forms. However, some countries, like the USA, have separated Cs whereas other countries, Japan and France, have suggested that as part of partitioning and transmutation strategy they will produce a Cs-rich waste stream. In order to reduce the impact of Cs escaping from high - Cs level waste forms and/or Cs-rich waste streams to the biosphere, long-term engineered barriers may be used. For these reasons it is useful to study waste forms and sorption materials to determine if Cs waste immobilization and barriers are effective.

Cesium-alumosilicates are of interest for immobilization of ^{137}Cs and ^{135}Cs from the Cs-rich and/or intermediate waste streams. The phases $CsAlSiO_4$, $CsAlSi_5O_{12}$ and $CsAlSi_2O_6$ (pollucite) have been particularly considered. The preparation of $CsAlSiO_4$ and $CsAlSi_5O_{12}$ has been described by Gallagher et al. (1977) and Ito (1976), respectively. Komarneni et al. (1978) studied the exchange behavior of synthetic alumosilicates and Černý (1979) discussed pollucite alteration from the point of view of waste disposal. Together with these and other materials, cementitious materials for Cs immobilization have been proposed. However, as Cs, in these latter materials, is bonded in the form of hydroxides, it may be difficult to prevent the release of Cs into water solutions (e.g. Bagosi and Csetenyi, 1997).

Two new mica phases, Cs-annite ($CsFe(II)_3(AlSi_3)O_{10}(OH)_2$) and Cs-tetra-ferri-annite ($CsFe(II)_3(Fe(III)Si_3)O_{10}(OH)_2$), were recently synthesized and structurally characterized (Mellini et al., 1996; Drábek et al., 1998; Comodi et al., 1999). These mineral analogues offer another potential way to efficiently immobilize radioactive Cs. Cs-tetra-ferri-annite, in particular, can be easily synthesized under hydrothermal conditions typical of an industrial-scale immobilization facility. Finally, Comodi et al. (1999) in their study of Cs-tetra-ferri-annite established that there was no detectable internal

strain for pressures of up to 39.4 kbar and temperatures of up to 435 °C. They further suggested that the structural crystal-chemistry of Cs-tetra-ferri-annite indicated that this phase might be a suitable candidate for Cs immobilization from the Cs-rich and/or intermediate waste streams.

To prevent soil contamination with Cs it may be necessary to use material that can sorb Cs from infiltrating contaminated water. Zeolites and clay minerals are typical engineered barrier materials used for isolation of radioactive wastes from the environment. Natural zeolites, e.g., ferrierite (Mimura et al., 1992) and clinoptilolite (Arcoya et al., 1996), as well as synthetic zeolites (usually obtained from fly ash) have been studied for sorption of Cs from water solutions (e.g. Alastuey et al., 1997; Weiping et al., 1996). Clay minerals and clays are probably the most frequently tested materials for Cs adsorption (e.g. Gutierrez and Fuentes, 1996; Oscarson et al., 1994; Miyahara et al., 1991; Cho et al., 1993; Khan et al., 1994). As these phases naturally occur in sediments, they may control immobilization and transport of ^{137}Cs and ^{135}Cs isotopes in water solutions (Smith and Comans, 1996). Kim et al. (1996a,b) studied several layer silicates (illite, montmorillonite and kaolinite) by NMR and XPS, determining that Cs is best sorbed in the montmorillonite interlayer. The preferential adsorption of Cs by illite was studied by Kim and Kirkpatrick (1997, 1998), and sorption of Cs in soils by Hsu et al. (1994) and by Hsu and Chang (1994).

In this study, the leachability of Cs from synthetic Cs-tetra-ferri-annite and $CsAlSiO_4$ have been measured. Additionally, results have been obtained for the effectiveness of sorption of Cs onto montmorillonite and zeolite. The former results provide data for the ability to immobilise Cs and the latter, the effectiveness of sorption media to control Cs releases to the environment. A combination of these materials provides the ability to handle Cs-rich wastes and to minimise any releases from a disposal site.

2. Experimental

2.1. Analytical methods

Bulk chemical analyses of solid samples were performed by X-ray fluorescence (SpectroLab). Cesium, Na, K, Mg and Ca in solids and leachates were determined by atomic absorption spectrometry (AAS, Unicam 969). Dissolved Si, Al and Fe concentrations in leachates were determined by ICP/OES (Jobin

Yvon 24). Control analyses of Si and Fe were done by photometric methods. An INEL X-ray powder diffractometer with a PSD 120 position sensitive detector, Ge monochromator and Cu Kα radiation was used to record X-ray patterns. The morphology of run products (coated with Au–Pd) was examined on a Tesla BS 340 scanning electron microscope.

The specific surface area of samples was determined by Sorptomatic (Carlo-Erba). The cation exchange capacity (CEC) of Na-montmorillonite and Na-zeolite was determined from $Cs^+ \leftrightarrow Na^+$ ion exchange (Zachara et al., 2002). Loss of ignition (LOI) was determined by gravimetry at 1000 °C.

2.2. Sample preparation

Four Cs-doped materials were prepared: Cesium-tetra-ferri-annite, $CsAlSiO_4$, Cs-exchanged montmorillonite and Cs-exchanged zeolite 13X. All samples were ground and milled using an agate rotary mill. The ground materials were then sieved to obtain the size fraction below 0.04 mm which

was used for Cs leaching studies. The X-ray powder diffraction patterns of all Cs-doped samples are given in Fig. 1.

2.2.1. Cs-tetra-ferri-annite

Cs-tetra-ferri-annite (Cs-TFA), ideally $CsFe(II)_3$-$Fe(III)Si_3O_{10}(OH)_2$ was prepared from a stoichiometric mixture of SiO_2, Fe_2O_3 and CsOH. This mixture was first reduced for 4 h in a H_2 atmosphere at a temperature of 600 °C. The starting material was then heated under hydrothermal conditions in a sealed Ag tube for 95 h at 600 °C and 100 MPa (Drábek et al., 1998). The run products consist of 99% TFA forming hexagonal plates and aggregates of mica flakes 30–60 μm in size (Photo 1), accompanied by a very small amount of magnetite and pollucite (Fig. 1a). The product contains 19.2 wt% Cs (the bulk chemical analysis is given in Table 1) and its specific area and CEC are less than the limits of detection, $LOQ = 0.4 \text{ m}^2 \text{ g}^{-1}$ and $LQQ = 0.03$ m-equiv g^{-1}, respectively, for the techniques used in this study.
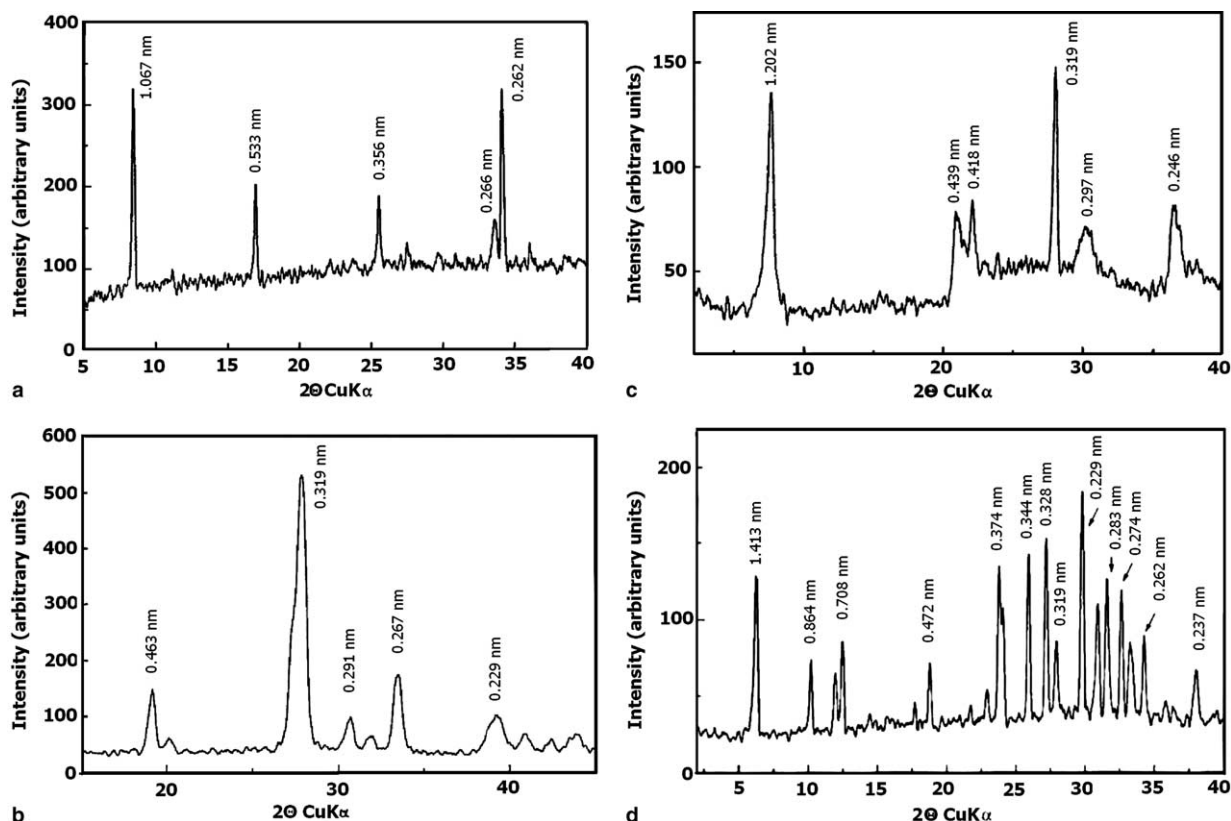

Fig. 1. XRD powder diffractions patterns of Cs-TFA (a), Cs-AS (b), Cs-MMT (c) and Cs-Z (d).
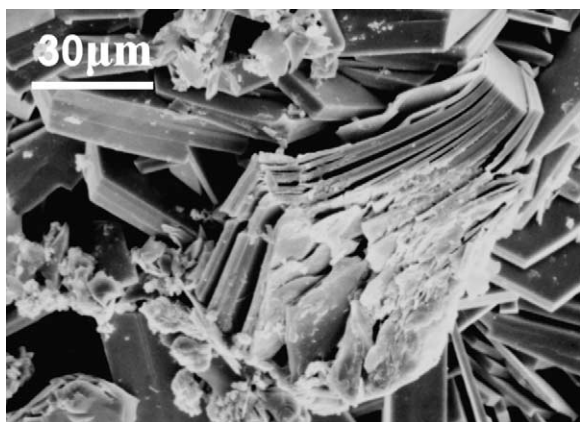
Photo 1. SEM photograph of synthetic Cs-TFA aggregates.

2.2.2. CsAlSiO₄

CsAlSiO₄ (Cs-AS) was synthesized from a stoichiometric mixture of Cs_2CO_3 and kaolinite $(Al_2Si_2O_5(OH)_4)$, heated for 12 h at 1100 °C in a Pt-crucible (Komarneni et al., 1978). The sample was repeatedly ground during synthesis. The reaction product is a white sintered powder that contains almost 100% CsAlSiO₄ (Fig. 1b) The bulk chemical analysis for the product is given in Table 1. The Cs content of the batch is 51.7 wt%, its specific area is 11.2 $m^2\,g^{-1}$ and CEC is equal to 0.10 m-equiv g^{-1}. The material prepared by Komarneni et al. (1978) had a smaller CEC (1.4 m-equiv 100 g^{-1}) and smaller surface area (3.2 $m^2\,g^{-1}$) than the material prepared in this study suggesting that the material used in this study may be more porous.

2.2.3. Cs-montmorillonite

Na-montmorillonite (Na-MMT) from Wyoming (USA) was used as the starting material for the preparation of Cs-exchanged montmorillonite (Cs-MMT). The product Cs-MMT is almost uncontaminated with other minerals (Fig. 1c). The structural formula for Na-MMT calculated from bulk chemical analyses (Table 1) is

$$Na_{0.41}K_{0.11}Ca_{0.05}(Mg_{0.47}Fe(III)_{0.49}Al_{3.05})$$
$$\times [Si_{7.78}Ti_{0.02}Al_{0.21}]O_{20}(OH)_4$$
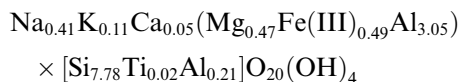
This formula is in agreement with that of Weaver and Pollard (1973). The Na-MMT used in these studies was air-dried, and the size fraction below 45 μm was separated. Cs-MMT was prepared by repeatedly contacting 0.2 g of Na-MMT with 100 cm^3 CsCl solution (500 mg Cs dm^{-3}) in 5 saturation steps. Each step consisted of 24 h of shaking, followed by separation using a centrifuge (5000 rpm for 30 min.), washing twice with deionized water and determination of sorbed Cs. After the final saturation step the sample was rinsed with deionized water until almost all the Cl^- ions were removed ($AgNO_3$ test); the sample was then air-dried. Cesium saturation values for Na-MMT after each saturation step are given in Table 2. The total Cs content in Cs-MMT is 8.83 wt% (the bulk chemical analysis of Cs-MMT is given in Table 1), the specific area is 136 $m^2\,g^{-1}$, and CEC is equal to 0.71 m-equiv g^{-1}. These values are similar to those quoted in Gutierrez and Fuentes (1996); viz. specific area of 80–84 $m^2\,g^{-1}$, and CEC is equal to 0.80–0.88 m-equiv g^{-1}.

Table 1
Bulk chemical analyses of Cs-tetra-ferri-annite (Cs-TFA), CsAlSiO₄ (Cs-AS), Na-montmorillonite (Na-MMT), Cs-montmorillonite (Cs-MMT), Na-zeolite 13X (Na-Z) and Cs-zeolite 13X (Cs-Z)

	Cs-TFA (%)	Cs-AS (%)	MMT		Z	
			Na-MMT (%)	Cs-MMT (%)	Na-Z (%)	Cs-Z (%)
SiO_2	29.94	25.27	57.80	53.44	46.05	37.27
TiO_2	<0.02	<0.02	0.16	0.16	0.02	0.02
Al_2O_3	0.21	19.85	20.25	18.87	27.22	21.79
Fe_2O_3	12.10	<0.01	4.89	4.54	<0.01	<0.01
FeO	34.52	<0.02	<0.02	<0.02	<0.02	<0.02
CaO	<0.05	<0.05	0.35	0.32	0.06	0.06
MgO	<0.24	<0.24	2.40	2.20	<0.24	<0.24
Na_2O	<0.05	<0.05	2.05	<0.05	11.52	3.84
K_2O	<0.02	<0.02	0.70	0.59	0.04	0.03
Cs_2O	20.32	54.87	<0.05	9.36	<0.05	24.84
(Cs)	(19.17)	(51.7)	–	(8.83)	–	(23.43)
LOI	2.92	<0.05	11.35	10.53	14.91	12.05
Total	100.01	99.99	99.95	100.01	99.82	99.87

Table 2
Cumulative saturation of Na-montmorillonite (Na-MMT) and Na-zeolite (Na-Z) by CsCl solution

	Na-MMT	Na-Z
	mg Cs $1g^{-1}$ Na-MMT	mg Cs $1g^{-1}$ Na-Z
1st saturation	81.0 ± 2.3	166.3 ± 4.3
2nd saturation	10.3 ± 0.5	77.5 ± 2.5
3rd saturation	3.0 ± 0.8	28.0 ± 2.5
4th saturation	0.4 ± 0.3	9.5 ± 4.0
5th saturation	–	1.5 ± 1.0
Total	94.7	282.8

2.2.4. Cs-zeolite 13X

Cs-zeolite (Cs-Z) was prepared from the commercially available Na-form of zeolite 13X (Na-Z) produced by Linde Air Products Company, USA. Na-zeolite was transformed into Cs-Z following the procedure described for Cs-MMT. The chemical composition of Na-Z 13X is given in Table 1; its SiO_2/Al_2O_3 molar ratio is equal to 2.8, similar to that of X-type zeolites (e.g. Kerr, 1981). Cs-Z contains 23.43% Cs (the bulk chemical analysis is reported in Table 1), its specific area is 465 $m^2 g^{-1}$ and CEC is equal to 2.13 m-equiv g^{-1}. X-ray powder patterns of the sample are given in Fig. 1d.

Na-Z adsorbed 282.8 mg Cs g^{-1} of Na-Z; Na-MMT adsorbed only 94.7 mg Cs g^{-1} Na-MMT (Table 2). The exchange of Na by Cs in Na-MMT was completed after 3 saturation steps. Five saturation steps were necessary for exchange in the Na-Z sample (see Fig. 2). In contrast with Na-MMT (in which all Na^+ ions were completely replaced by Cs^+ ions), only two-thirds of the Na initially present in Na-Z was exchanged for Cs after saturation, i.e.
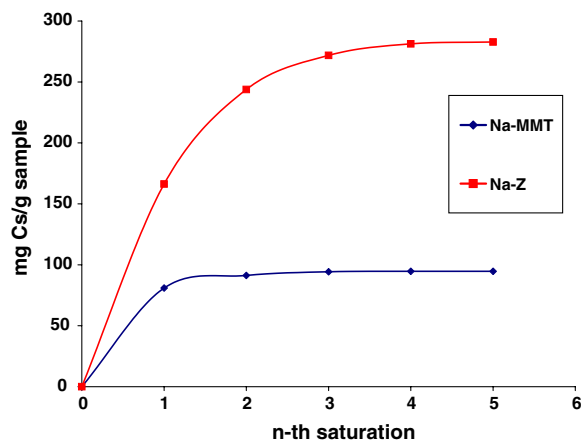

Fig. 2. Cumulative saturation of Na-montmorillonite (Na-MMT) and Na-zeolite 13X (Na-Z) with CsCl.

3.84 wt% Na_2O was not exchanged. According to Haynes (1978) Na^+ ions embodied in the smallest cavities of Na-Z are the most difficult to extract from the framework and be replaced by Cs^+ ions because of the very small zeolite diameter opening (approximately 0.25 nm).

The sorption studies show that the MMT phase absorbs about 2.7 times less Cs, based on solid analysis (Table 1), and about 3.0 times less, based on solution analyses (Table 2), than the Z phase.

2.3. Leaching methods

Cesium was extracted from the Cs-doped materials through two different batch leaching procedures and continuous leaching in a Soxhlet extractor. Batch leaching was used to study Cs-leaching at different temperatures (20 and 100 °C). In this method, the samples are always in contact with the leachate. In contrast, during leaching in the Soxhlet extractor, the samples are repeatedly leached with condensed steam at a temperature of about 72 °C .

2.3.1. Batch leaching at ambient temperature (method A)

Leaching was carried out by adding 100 cm^3 of deionized water to 100 mg of solid sample. The pH of the suspension was adjusted to pH 3 by adding drops of 0.5 M HCl, or to pH 11 by adding drops of 0.5 M NaOH, respectively. The samples were shaken for 24 h in a closed vessel at ambient temperature. During this time, pH values were corrected twice (after 1 h and 8 h of shaking); without adjustment the pH was close to 7 except for Cs-Z (pH about 9). The pH of the Cs-Z suspension was adjusted to about pH 7 by adding drops of 0.1 M HCl. Finally, the solid samples were centrifuged at 5000 rpm for 30 min, the supernatants filtered through micro filter Pragopor 5 (0.60 μm) and the Cs content determined by AAS.

2.3.2. Batch leaching under reflux (method B)

The sample (100 mg in weight) was kept at boiling point (100 °C) with 100 cm^3 of deionized water in a boiling flask equipped with a water cooler. After a boiling period of 24, 80 and/or 160 h, the suspension was cooled to laboratory temperature, and the solid phase was separated by centrifugation at 5000 rpm for 30 min. The supernatant was filtered through micro filter Pragopor 5 (0.60 μm), pH was measured and the Cs concentration was determined by AAS. Sodium, Al, Si and total Fe

were also determined in leachates from the 80 h experiments.

2.3.3. Continuous leaching (method C)

A 100 mg sample was leached in a Soxhlet extractor (Fig. 3) using 100 cm^3 of deionized water. During leaching, water evaporates from the boiling flask (1) of the extractor; the vapor rises through a wide, parallel side tube (2) and condenses in the water bulb condenser (3). Water then fills the thimble containing the solid sample (4) and leaches it. After the water level reaches the high level extraction siphon (5), the leachate overflows into the boiling flask. This cycle is repeated many times. During the leaching experiments the temperature in the thimble varied from 70 to 74 °C. Leaching was performed over 24- or 48-h periods. The supernatant from the boiling flask was passed through microfilter Pragopor 5 (0.60 μm), and the pH and Cs concentration were measured.
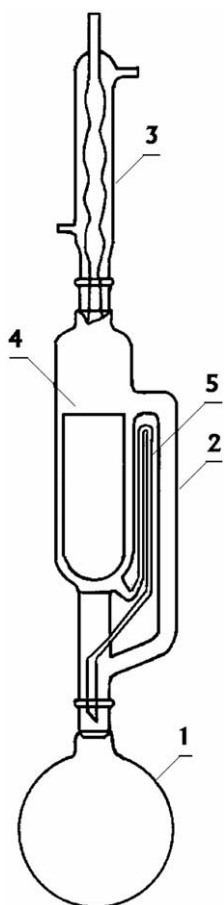

Fig. 3. Soxhlet extractor.

3. Results

Cs-TFA, Cs-AS, Cs-MMT and Cs-Z were tested for Cs removal by water leaching. The weight fraction of leached Cs from Cs-forms, w_{Cs} (mg g^{-1}), was calculated from the formula:

$$w_{Cs} = \frac{c.V}{m} \tag{1}$$

where c is the concentration of Cs in solution after leaching (mg cm^{-3}), V the volume of solution added (cm^3), and m is the weight of the Cs-form sample before leaching (g).

If the weight fraction of Cs in a sample before leaching is w_s (mg g^{-1}), the percentage of leached Cs with respect to total Cs in the original sample, Cs (wt%), can be calculated from the formula:

$$Cs\ (wt\%) = 10^2 \frac{w_{Cs}}{w_s} \tag{2}$$

Many authors (e.g. Hsu and Chang, 1994; Sinha et al., 1995) adopt the distribution constant K_d (cm^3 g^{-1}) to characterize Cs adsorption and/or desorption. The distribution constant, K_d can be defined as:

$$K_d = \frac{w_s^*}{c^*} \tag{3}$$

where w_s^* (mg g^{-1}) is the Cs weight fraction in the sample and c^* (mg cm^{-3}) is the concentration of Cs in solution after adsorption or desorption, respectively. Then K_{da} and K_{dd} in the text refer to K_d values determined by adsorption and desorption (leaching), respectively.

3.1. Batch leaching at ambient temperature (method A)

Batch leaching of all Cs-doped samples at ambient temperature and under different pH conditions was carried out in triplicate to check reproducibility. The results are presented in Table 3. This Table reports: (a) the Cs weight fraction in the sample before leaching (w_s), (b) the mean values of the weight fractions of leached Cs (w_{Cs}), including the data measurement intervals, and (c) the weight percentages of (Cs, wt%) leached from the solid. The w_{Cs} values were calculated from Eq. (1) using the measured Cs concentration in solution after leaching (c). Leaching was performed using 100 cm^3 (V) of leaching solution and 100 mg (m) Cs-samples. The Cs (wt%) leached out from the solid samples was calculated from Eq. (2).

Table 3
Effect of pH on the leaching of Cs at ambient temperature (measured using method A)

Samples	w_s (mg/g)	pH 3		Unadjusted		pH 11	
		w_{Cs} (mg/g)	Cs (wt%)	w_{Cs} (mg/g)	Cs (wt%)	w_{Cs} (mg/g)	Cs (wt%)
Cs-TFA	191.7	1.00 ± 0.11	0.52	0.54 ± 0.08	0.28	2.72 ± 0.11	1.42
Cs-AS	517.0	31.1 ± 8.2	6.01	5.33 ± 1.10	1.03	11.2 ± 1.7	2.17
Cs-MMT	88.3	31.3 ± 1.5	35.5	1.98 ± 0.23	2.24	18.4 ± 2.4	20.8
Cs-Z	234.3	198 ± 16	84.5	6.16 ± 1.03	2.63	28.8 ± 3.4	12.3

The percentage of Cs leached from the solid samples Cs (wt%) is plotted in Fig. 4. The lowest Cs removal occurred for Cs-TFA, followed by Cs-AS, Cs-MMT and Cs-Z. Cesium removal from each sample differed under the various pH leaching conditions; it was higher in acid (pH 3) or alkaline environments (pH 11) than in neutral environments (about pH 7). The highest Cs removals were from Cs-MMT and Cs-Z, both in acid and alkaline environments. In alkaline solution, the high Cs removal for these latter phases can be explained by partial replacement of Cs^+ by Na^+ ions, given that the pH 11 was adjusted through the addition of NaOH. Recently, Dumat et al. (2000) made a similar observation. The presence of Na^+ ions in solution influences Cs removal from Cs-AS and Cs-TFA to a much lower extent.

The small effect of pH on release rates of Cs from Cs-TFA is typical of ceramic-type materials with low porosity and surface area (Ringwood et al., 1988). The intermediate behaviour of Cs-AS reflects that this material has a lower CEC and specific area than Cs-MMT and Cs-Z. Releases of Cs from Cs-AS are slightly larger than those measured by Komarneni et al. (1978) under ambient temperature
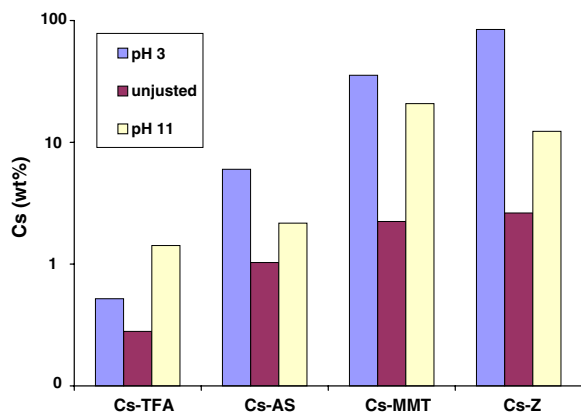
in deionised water. The slightly larger releases from this waste form in the current study may reflect the effect of the higher surface area and CEC values for the material prepared. Generally, the releases from the four materials increase with increasing specific area and CEC reflecting the availability of surface sites for reaction.

3.2. Batch leaching under reflux (method B)

The batch technique was also used to evaluate Cs leaching from Cs-samples under reflux. Three different time-regimes were applied:

- 24 h leaching at 100 °C,
- two 80 h leaching periods at 100 °C,
- 160 h leaching at 100 °C.

A 100 mg sample and 100 cm^3 of deionized water were used for the 24 h leaching regime and the procedure was carried out in triplicate. A new 100 mg sample and a fresh 100 cm^3 of deionized water were used for the first 80 h leaching period (1). After the first 80 h of leaching (period 1), the same solid sample was leached for another 80 h (period 2) with a fresh 100 ml portion of deionized water. The 80 h leaching experiments were carried out on individual samples. For individual samples (0.100 g) the 160 h control leaching experiments were carried out with 100 cm^3 of deionized water. The weight fraction of leached Cs from Cs-forms, w_{Cs} (mg g^{-1}) after 160 h of leaching is very similar to the sum of w_{Cs} (mg g^{-1}) from the first and the second 80 h leaching periods.

The percentage of Cs leached from the solid samples, Cs (wt%), for 24 h and two 80 h periods are reported in Table 4. The Cs-TFA is the phase with the lowest removal of Cs in all of the test periods. After 24 h, releases of Cs from Cs-TFA are lower, by factors of between 3.9 and 7.6, than those from the other 3 materials. In the two 80 h leach periods, the lowest releases were obtained from Cs-TFA.

Fig. 4. The effect of pH on release of Cs from Cs-TFA, Cs-AS, Cs-MMT and Cs-Z (measured using method A at ambient temperature).

Table 4
Effect of contact time on the release of Cs into deionized water under reflux (measured using method B)

Samples	24 h			80 h (period 1)		80 h (period 2)		160 h
	w_{Cs} (mg/g)	Cs (wt%)	pH	w_{Cs} (mg/g)	Cs (wt%)	w_{Cs} (mg/g)	Cs (wt%)	w_{Cs} (mg/g)
Cs-TFA	2.15 ± 0.06	1.12	6.84	6.52	3.40	4.87	2.54	10.5
Cs-AS	43.9 ± 8.2	8.50	8.75	104	20.1	53.3	10.3	156
Cs-MMT	3.89 ± 0.50	4.40	7.75	11.6	13.1	5.00	5.66	17.2
Cs-Z	14.5 ± 2.2	6.20	9.18	37.7	16.1	31.4	13.4	62.0

The results for the Cs-MMT and Cs-Z materials followed a similar trend to the Cs-TFA phase. The releases from the Cs-MMT were marginally lower than from the Cs-Z although for the latter material the Cs release in the second 80 h leach period did not decrease by as much.

As shown in Table 4, the Cs releases over the first 80 h period, for all the samples, are between factors of 2.4 and 3 higher than those from the 24 h leach period. Cesium releases measured over the second 80 h leach period (Table 4) decreased from those measured in the first 80 h period by factors of about 1.2–2.3, but were still elevated above those for the 24 h test by factors of 1.2–2.3. Taking into account that 80 h periods are 3.3 times longer than 24 h periods it appears that Cs releases decrease with contacting time. A decrease of Cs-leaching rate with contacting time (at different temperatures) was also found by Ringwood et al. (1988) for leaching tests with Synroc used for HLW immobilization.

3.3. Continuous leaching (method C)

Two different time regimes were used for the continuous leaching test:

- 24 h leaching,
- two 48 h leaching periods.

Results for the continuous leaching of Cs are given in Table 5, with data arranged as in Table 4. Sample weight, m (100 mg) and deionized water volume, V (100 cm^3) were used as before. For both the 24 h and the first 48 h leaching periods, new sample and fresh water were used. After the first 48 h leaching (period 1), the solid samples were leached for another 48 h (period 2) with a new 100 ml portion of deionized water. In the case of the 24 h leaching period, the procedure was carried out in triplicate; in the case of the two 48 h periods, the measurements were made on a single sample.

Under these experimental conditions, much less Cs is leached from Cs-TFA than from the other phases in all of the test periods. After 24 h it is lower, by factors between 2.8 and 7.4, than that for the other three materials. In contrast, the releases of Cs from Cs-AS are higher than that of all the other phases. The removal of Cs from the Cs-MMT and Cs-Z materials was higher by factors between about 1 and 7 over all leach periods than that for Cs-TFA. The ratio between Cs leached from the solid samples, Cs (wt%) in the first 48 h period and in 24 h period varies from 1.5 to 2.0. If the results for the samples leached for 24 h and the first 48 h period are compared, then it appears that under these experimental conditions that the leaching rate decreases with contact time for the high temperature phases. However, releases of Cs from Cs-MMT and Cs-Z phases, under these experimental conditions are nearly proportional to the increase in contact time.

By comparing the results of Cs removal after 24 h using different methods (A, B and C), it is concluded that the lowest Cs removal is from Cs-TFA, under all experimental conditions (Fig. 5). In the ambient temperature batch leaching tests (method A),

Table 5
Effect of time on the releases of Cs into deionized water measured using a Soxhlet extractor and method C at temperatures between 72 to 74 °C

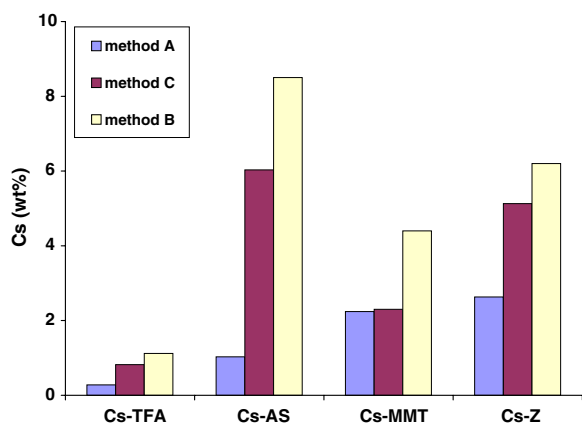| Samples	24 h			48 h (period 1)		48 h (period 2)	
	w_{Cs} (mg/g)	Cs (wt%)	pH	w_{Cs} (mg/g)	Cs (wt%)	w_{Cs} (mg/g)	Cs (wt%)
Cs-TFA	1.57 ± 0.13	0.82	7.05	2.68	1.40	2.63	1.37
Cs-AS	31.2 ± 3.2	6.03	8.66	46.0	8.90	23.3	4.51
Cs-MMT	2.03 ± 0.20	2.30	6.75	3.97	4.50	1.80	2.04
Cs-Z	12.0 ± 1.0	5.13	9.08	22.3	9.50	12.9	5.51

Fig. 5. The effect of leaching methods, A, B and C, on releases of Cs from Cs-TFA, Cs-AS, Cs-MMT and Cs-Z.

releases increase from Cs-AS to Cs-MMT and Cs-Z, namely, Cs removal is highest for Cs-Z. Conversely, the leachability order changes in the other leaching methods (B and C), because of the high thermal dependence of the leaching of Cs from Cs-AS. Leachability for the Cs-MMT sample is least dependent on temperature. Therefore, Cs-MMT also appears appropriate for Cs sorption at high temperatures and in flow systems. Hsu and Chang (1994) attribute this stability to Cs sorption in the montmorillonite interlayer sites.

3.4. Batch leaching of Si, Al, Fe and Na under reflux

Cesium might be extracted from the solid sample either by partial dissolution of the entire sample, and/or by selective Cs leaching from the material. To investigate these alternatives, additional measurements were made on both the leached solid samples and the leachates produced using method B (see Section 3.2). Batch leaching at the boiling point was selected because this method led to the greatest removal of Cs.

X-ray diffraction patterns of initial and 160 h leached solid samples (after duplicate 80 h leaching) were recorded and the patterns matched exactly. In the leached samples, no other diffraction patterns belonging to new crystalline phases were observed. These results are comparable to those of Berger et al. (1988) who studied zeolite, chlorite and smectite that were formed by precipitation from various glasses in water solutions of different composition at temperatures from 50 to 300 °C. In Berger's work, the diffraction patterns of newly formed phases were recorded mostly at temperatures above 100 °C, at

lower temperatures where new phases were present they were poorly crystallized.

The 80 h leachates (periods 1 and 2) were analyzed for Cs, Si, Fe, Al and Na. The weight fractions of leached elements from the Cs-samples (w_i) are reported in Table 6; Cs analyses were taken from Table 4.

By summing the leached elements, the percentage of the sample that had dissolved was estimated. These percentages are: 1.1% and 2.0% for Cs-TFA, 11.9% and 18.6%, for Cs-AS, 2.0% and 3.1% for Cs-MMT and for Cs-Z 5.3%, 10.0% after 80 and 160 leaching h, respectively. No changes in X-ray diffraction patterns and no observable changes in the morphology of all samples (SEM) were observed after 160 h of leaching at a temperature of 100 °C.

In order to compare the proportion of elements extracted from solid to leachate, molar ratios between these elements and Si were calculated. A similar approach was used by Berger et al. (1988) in their kinetic study of glass dissolution. Table 7 lists the molar ratios after the 1st (MR-1) and 2nd leaching (MR-2) calculated from the data in Table 6. In addition, the molar ratio of elements in the original solid (FMR) was calculated from the bulk chemical analyses of Table 1, the Fe_{total} content was calculated from percentages of FeO and Fe_2O_3 oxides. Calculated FMR and MR values for all Cs-samples are reported in Table 7.

The Cs/Si ratio in Cs-TFA leachates is approximately the same after the first 80 h leaching (MR-1) and the second 80 h leaching (MR-2). Neither ratio differs from FMR. The Cs and Si removals are here equivalent, thus suggesting congruent dissolution

Table 6
Leached Na, Cs, Al, Fe_{tot} and Si from Cs-forms of samples (100 °C, method B)

Samples	Time of leaching (h)	w_i (mg/g)				
		Na	Cs	Al	Fe_{tot}	Si
Cs-TFA	80 (1)	–	6.52	–	0.05	4.50
	80 (2)	–	4. 87	–	0.05	4.01
Cs-AS	80 (1)	–	104	1.60	–	13.0
	80 (2)	–	53.3	2.20	–	12.0
Cs-MMT	80 (1)	0.80	11.6	0.05	–	8.20
	80 (2)	0.40	5.00	0.06	–	6.52
Cs-Z	80 (1)	2.00	37.7	9.30	–	6.20
	80 (2)	2.40	31.4	9.20	–	6.01

Note: (1) The first 80 h water leaching period. (2) The second 80 h water leaching period for the sample already leached for 80 h (1).

Table 7
Molar ratios of major elements to Si in Cs-analogues (FMR) and in leachates (MR-1 and MR-2)

Samples	w_i/w_{Si} (mmol/mmol)					
	Mass ratios	Cs/Si	K/Si	Na/Si	Al/Si	Fe_{total}/Si
Cs-TFA	FMR	0.30	–	–	1.26
	MR-1	0.30	–	–	0.01
	MR-2	0.25	–	–	0.01
Cs-AS	FMR	0.93	–	0.93
	MR-1	1.69	0.12
	MR-2	0.93	0.19
Cs-MMT	FMR	0.074	<0.002	0.42
	MR-1	0.30	0.12	0.006
	MR-2	0.16	0.07	0.009
Cs-Z	FMR	0.27	0.20	0.69
	MR-1	1.29	0.39	1.6
	MR-2	1.10	0.49	1.6

Notes: FMR, formula molar ratio, calculated from chemical analysis of solid sample (Table 1) MR-1, molar ratio of elements in the first 80 h water leachate (100 °C, method B, Table 6); MR-2, molar ratio of elements in the second 80 h water leachate (100 °C, method B, Table 6).

of these elements from the Cs-TFA phase. In contrast, very low Fe/Si values were found for MR-1 and MR-2 (Table 7), indicating that Fe is associated with the solid either sorbed onto the surfaces or strongly bonded in the sample even after 160 h of leaching.

For Cs-AS, the Cs:Si ratio in the leachate is higher than the FMR in the first 80 h period (MR-1) while the MR-2 Cs/Si ratio is similar to FMR. In contrast, removal of Al is much less than for Cs and Si during both leaching periods.

For Cs-MMT, the Cs:Si ratio is 4 and 2 times higher than the FMR, after the first 80 h and the second 80 h, respectively. The very low Al/Si ratios (MR-1 and MR-2) show that Al is hardly leached at all. Mukhamet-Galeyev et al. (1995) came to the same conclusion during the study of Si, Al, Mg and Ca leachability from Ca–Mg bentonite. In agreement with the present results, they also observed the non-equilibrium character of leaching, i.e. ongoing removal of all elements with increasing duration of leaching.

Of all the samples, Cs-Z shows the largest Cs/Si ratios in leachates (see MR-1 and MR-2 in Table 7). Ratios are approximately four times larger than the FMR value. In contrast to Cs-AS and Cs-MMT samples, the Al/Si ratios (see MR-1 and MR-2 in Table 7) are more than 2 times higher than FMR, i.e. Al is here more easily removed than Si. The easy

removal of Al from zeolites at higher temperatures and in acid solutions was also reported by Haynes (1978).

4. Discussion

The overall stability of the Cs-TFA phase under all leaching conditions used in this study indicates that this material is a low porosity, durable ceramic-like waste form that could be used to immobilize Cs. The low and congruent release of Cs and Si at 100 °C shows that the structure of the material is controlling releases as expected for Cs isolated within a ceramic-like structure.

Komarneni et al. (1978) also studied the Cs-AS phase as a candidate for Cs immobilization. They measured percentage of Cs releases into deionised water over 24 h at ambient temperatures of 0.73 (wt%), which is slightly less than the release measured in this study of 1.03 (wt%). The lower result in Komarneni et al.'s work may arise from the smaller surface area (3.2 m² g⁻¹) and CEC for their material (0.014 meq g⁻¹) or the higher solid to liquid ratio (8 g dm⁻³) that was used in their study possibly resulting in saturation effects. In their work, they found that the release of Cs was associated with congruent release of Si suggesting that releases resulted from the breaking of aluminosilicate bonds and release of Cs from the surface. Although the Cs release measured in the present study in the first contact at 100 °C had preferential release of Cs over Si in the second contact the releases were congruent suggesting that, in agreement with the suggestion of Komarneni et al. (1978) that after surface Cs is released continuing releases are controlled by congruent dissolution. Komarneni et al. (1978) also noted that this phase compared well with other phases being studied for Cs immobilization, however they also noted that further work was required to ascertain the effect of temperature of leaching on the stability of this phase. The detrimental effect of higher temperature leaching on Cs release obtained in the present study for Cs-AS suggests that this material is not as suitable for Cs immobilization as Cs-TFA.

Komarneni and Roy (1978) found that heating Cs saturated illites to temperatures exceeding 750 °C drastically reduced de-sorption of Cs by factors of between about 8 and 1.4. Ritherdon et al. (2003) found a similar effect with U-doped montmorillonite and muscovite with U extraction dropping to negligible levels after heat treatment to temperatures of

around 500–600 °C. These authors attributed the reduction in releases to the onset of dehydroxylation indicating that decomposition and collapse of the clay mineral structure results in stronger retention of U. These findings are in agreement with the results obtained in this study for Cs-AS and Cs-TFA at ambient temperature and as a function of pH as under these conditions the releases of Cs are much lower than those from Cs-MMT and Cs-Z. The poor performance of Cs-AS at elevated temperatures suggests that the advantages of preparing the phase at high temperatures has almost disappeared when Cs-AS is in contact with water at 100 °C.

For the phases, which sorb Cs from water solutions (MMT and Z), the distribution coefficients K_d were calculated from Eq. (3). The K_{da} values were calculated from the first saturation of Na-MMT and Na-Z (Table 2) by CsCl water solution (500 mg Cs dm^{-3}), while K_{dd} values were calculated using desorption (leaching) data presented in Tables 3 and 4. The K_{dd} values for the second 80 h period were calculated by adjusting the value for w_s (Eq. (3)) to take account of Cs removed in the first 80 h leaching period (76.7 mg g^{-1} for Cs-MMT and 196.6 mg g^{-1} for Cs-Z). All distribution coefficients are given in Table 8.

The greatest difference among K_d values is between K_{da} and K_{dd} data. For ambient temperature and a 24 h period the ratio K_{dd}/K_{da} is 183 for MMT and 37 for Z, showing that Cs is much better adsorbed than desorbed. The calculated $K_{da} = 2.4 \times 10^2$ cm^3 g^{-1} and $K_{dd} = 4.4 \times 10^4$ cm^3 g^{-1} for Cs-MMT (Table 8) are comparable to data ($K_{da} = 2.97 \times 10^3$ cm^3 g^{-1} and $K_{dd} = 1.94 \times 10^4$ cm^3 g^{-1}) of Hsu and Chang (1994) determined for Ca–bentonite.

The effect of experimental conditions on the distribution coefficient (K_{dd}) was recently discussed by Dumat et al. (2000). In their work, they showed that this coefficient varied with: the ionic strength of the solution and its pH, the leaching solution volume, sample mass, time and temperature of leaching and competition between elements in solution. The

present leaching (desorption) experiments also show that Cs equilibrium between solution and fresh Cs-doped materials (Cs-MMT and Cs-Z) is not reached during the 24 h test at 100 °C, because the K_{dd} values calculated from the 24 h and the first 80 h tests, under the same experimental conditions are decreased by about a factor of 3. It can be also supposed that with decreasing content of Cs in MMT and Z the K_{dd} values will decrease as well. For example, Berger (1992) studied distribution of Cs and some other elements in three Fe, Mg smectites, three Na-zeolites and three Fe, Mg-chlorites containing 58–128 ppm, 103–308 ppm and 33–48 ppm of Cs, respectively. The concentration of Cs in the starting solutions used for K_{dd} determination varied from 2 to 10 mg kg^{-1} and the experiments were run at ambient temperature and used a water/rock ratio of 4. The determined Cs distribution coefficients (K_{dd}) were 14, 40 and 5.7 for Fe, Mg smectites, Na-zeolites and Fe, Mg-chlorites, respectively.

The data for leaching over a 24 h period at temperatures of 20, 72 and 100 °C were used to construct an Arrhenius plot for the 4 Cs-doped samples (Fig. 6). For this, the Cs leaching rate from solid into leaching solution (given as g Cs m^{-2} day^{-1}) was used as an index of total leachability (e.g. Ringwood et al., 1988). The activation energies (E_a (kJ/mol)) obtained were 15.9, 24.7, 6.3, 9.9 for Cs-TFA, Cs-AS, Cs-MMT, Cs-Z, respectively. The data for Cs-TFA and Cs-AS are similar to values of about 15–30 kJ/mol obtained previously for ceramic-type phases (Trocellier, 2001; Ringwood et al., 1988). The highest activation energy of Cs-AS confirms the greatest dependence of this material on the temperature of leaching. The lower values for Cs-MMT and Cs-Z, although not highly significant, suggest a different mode of leaching for these materials compared to Cs-TFA and Cs-AS. For Cs-MMT and Cs-Z, it would be expected that the dominant release mechanism would be by ion exchange and the activation energies calculated for these materials are in the range that Atun et al. (1996) quote

Table 8
Adsorption (K_{da}) and desorption (K_{dd}) distribution coefficients for Cs on MMT and Z phases

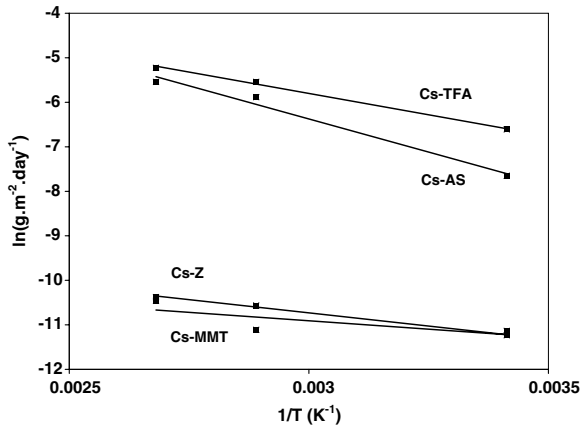|	K_{da} (cm^3 g^{-1})	K_{dd} (cm^3 g^{-1})			
		20 °C, method A, 24 h	100 °C, method B		
			24 h	80 h (period 1)	80 h (period 2)
MMT	2.4×10^2	4.4×10^4	2.2×10^4	6.6×10^3	1.4×10^4
Z	9.9×10^2	3.7×10^4	1.5×10^4	5.2×10^3	5.3×10^3

Fig. 6. Arrhenius plots of the leach rate of Cs from tested samples in deionized water at 20, 72 and 100 °C.

for ion exchange, i.e. typically from 8 to 16 kJ/mol. These values are also in good agreement with the activation energy E_a of Cs leach from Fe, Mg smectite (2.1 kJ/mol) and Na-zeolite (10.0 kJ/mol) that were calculated from Arrhenius plots presented by Berger et al. (1988).

The Cs leaching rate is often used as an index of the element leachability from the solid. Using the present data (Table 4) the leaching rates 3.91×10^{-3}, 2.86×10^{-5} and 3.11×10^{-5} g Cs m^{-2} day^{-1} were calculated for Cs-AS, Cs-MMT and Cs-Z, respectively. With reference to specific area of less than 0.4 m^2 g^{-1} the leaching rate $<5.38 \times 10^{-3}$ g Cs m^{-2} day^{-1} was also calculated for Cs-TFA. In review of amorphous and crystalline solids considered as potential host matrices for immobilization of long-lived radionuclides, Trocellier (2001) showed also the data for the leaching rate of Cs. For crystalline materials the leaching rate typically varies from about 0.5 to 2.5 g Cs m^{-2} day^{-1} (e.g. for nepheline and hollandite) to about 1×10^{-3}–1×10^{-5} g Cs m^{-2} day^{-1} (e.g. for alkali-borosilicate glass and Synroc monolith, 90 °C), respectively. Leaching rates of amorphous forms of some ceramic materials can be about factor of 10–100 times higher, e.g. monazite and zircon (Trocellier, 2001). Ringwood et al. (1988), who studied leaching of Cs and many other elements from Synroc, showed that at 70–150 °C the starting Cs leaching rate from this material (prepared by cold-pressing and sintering) decreases after 80 days of leaching from 0.1 g Cs m^{-2} day^{-1} to 10^{-4} g Cs m^{-2} day^{-1}, i.e. by a factor of almost 1000. This comparison also shows that high temperature material Cs-TFA used in this work is comparable

with previous ones and can be used as a potential host matrix for Cs immobilization.

In order to predict the performance of wastes in leach processes mechanistic leach models are often used (Bourg and Kedziorek, 1998). Short-term leachability studies of low-level radioactive wastes showed that diffusion is a dominant factor controlling the leaching rate. A number of leach models have been suggested. The simplest and most commonly used model supposes that at the start of solid sample leaching the distribution of leached element is homogeneous, that no reactions occur and the slab is infinite. Such a type of leach model is also used for the evaluation of the standard dynamic leach test (ANS-16.1, 1986). For the evaluation of the authors' kinetic data, Eq. (4) of Godbeen and Joy (1974) diffusion model was used.

$$10^{-4} \cdot \frac{c_n \cdot V^2}{w \cdot S \cdot m^2} = \frac{2}{\pi} \sqrt{D_e \cdot t_n} \qquad (4)$$

where c_n is the concentration of Cs in water solution (mg cm^{-3}) obtained in the nth period of leaching, V is the volume of water solution (cm^3), m is the initial amount of leached sample (g) and w is the initial weight fraction of Cs in the leached sample (mg g^{-1}), S surface area (m^2 g^{-1}), D_e effective diffusion coefficient (cm^2 h^{-1}) and t_n total time (h) of leaching in the nth period.

Eq. (4) was also used by Cheng and Bishop (1990) who interpreted kinetic data obtained from serial leaching experiments of cement dust and lime fly ash with different strengths of acetic acid solution and Batchelor (1990) modified this model to describe the effect of inward diffusion of the leaching agent. Eq. (4) can be simplified into the form:
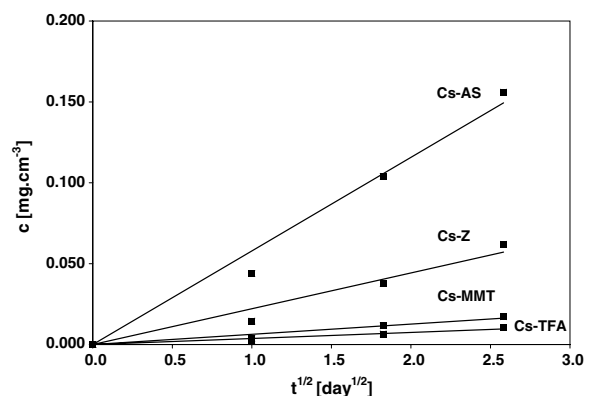

Fig. 7. Regression plots of the dissolved Cs from tested samples in deionised water at 100 °C versus time of leaching.
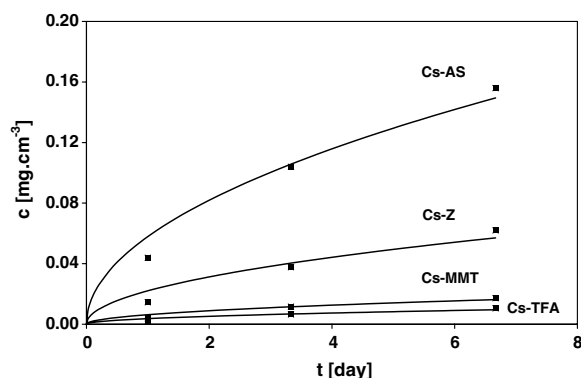
Fig. 8. Calculated and experimental leach rate of Cs from tested samples in deionised water at 100 °C.

$$c_n = k.\sqrt{t_n} \tag{5}$$

where k is the coefficient for each Cs mineral $(k = \frac{2 \times 10^4 \cdot m^2 \cdot w \cdot S}{\pi \cdot V^2}\sqrt{D_e})$.

For the evaluation of coefficient k in Eq. (5) the 24 h, 80 h (period 1) and 160 h data obtained for leaching of Cs-TFA, Cs-AS, Cs-MMT and Cs-Z at 100 °C (Table 4) were used. The regression functions (Eq. (5)) are plotted in Fig. 7. The calculated coefficients k are: 0.0037 for Cs-TFA, 0.0063 for Cs-MMT, 0.0221 for Cs-Z and 0.0579 for Cs-AS (all data in mg cm^{-3} day$^{-0.5}$). The decreasing rate of Cs dissolution from Cs doped samples can be seen in Fig. 8. This decrease is brought about by the gradually decreasing Cs concentration gradient between leachate and leached sample as predicted from Fick's first law.

5. Conclusions

The structural considerations that suggested that the high structural stability of Cs-tetra-ferri-annite would result in limited Cs leachability have been fully confirmed by leachability tests. This phase has demonstrated a high degree of Cs retention as a function of pH and over temperatures from ambient to 100 °C, thus suggesting that it is a possible candidate phase for Cs immobilization. Further work to establish its radiation stability and long-term durability are still required. CsAlSiO$_4$ that was tested as a reference material to Cs-tetra-ferri-annite as a potential host matrix for Cs immobilization showed under all conditions (pH from 3 to 10, leaching temperature from ambient to 100 °C) higher Cs release. Most importantly CsAlSiO$_4$ releases Cs into water at increased temperature.

Montmorillonite saturated with Cs (Cs-MMT) exhibits limited Cs-leachability at ambient temperatures with no increase in release at temperatures up to 72 °C. Cesium release from Cs-MMT is less then that from Cs-zeolite 13X.

The authors therefore envisage a possible scenario for the treatment of Cs wastes involving the coupled use of tetra-ferri-annite and montmorillonite. Cesium-tetra-ferri-annite might be suited to fix Cs from Cs-rich or intermediate waste streams within a crystalline, solid matrix and Na-montmorillonite might be used as an outer, barrier capable of buffering the possible escape of Cs, even under varying pH conditions and increasing temperatures.

Acknowledgements

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